

ELECTROLYSIS CELL FOR GENERATING HALOGEN (AND PARTICULARLY
CHLORINE) DIOXIDE IN AN APPLIANCE

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CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation in part of United States Application Serial Number 09/947,846, filed on 06 September 2001.

FIELD OF THE INVENTION

This invention relates to devices for generating halogen dioxide, preferably chlorine dioxide, from aqueous solutions containing a halogen dioxide salt, preferably chlorite salts, suitable for interface with an appliance, and particularly a refrigerator.

BACKGROUND OF THE INVENTION

Chlorine dioxide, ClO_2 , is one of the most effective bleaching agents for use in industrial and domestic process and services, and for commercial and consumer products. The strong oxidative potential of the molecule makes it ideal for a wide variety of uses that include disinfecting, sterilizing, and bleaching. Concentrations of chlorine dioxide in an aqueous solution as low as 1 part per million (ppm) or less, are known to kill a wide variety of microorganisms, including bacteria, viruses, molds, fungi, and spores. Higher concentrations of chlorine dioxide, up to several hundred ppms, provide even higher disinfection, bleaching and oxidation of numerous compounds for a variety of applications, including the paper and pulp industry, waste water treatment, industrial water treatment (e.g. cooling water), fruit-vegetable disinfection, oil industry treatment of sulfites, textile industry, and medical waste treatment.

Chlorine dioxide offers advantages over other commonly used bleaching materials, such as hypochlorite and chlorine. Chlorine dioxide can react with and break down phenolic compounds, and thereby removing phenolic-based tastes and odors from water. Chlorine dioxide is also used in treating drinking water and wastewater to eliminate cyanides, sulfides, aldehydes and mercaptans. The oxidation capacity of ClO_2 , in terms of available chlorine, is 2.5 times that

of chlorine. Also, unlike chlorine/hypochlorite, the bactericidal efficiency of chlorine dioxide remains generally effective at pH levels of 6 to 10. Additionally, chlorine dioxide can inactivate *C. parvum* oocysts in water while chlorine/hypochlorite cannot. Hypochlorite and chlorine both react with the bleached target by inserting the chlorine molecule into the structure of the target.

5 Though this mode of reaction can be effective, it can result in the formation of one or more chlorinated products, or by-products, which can be undesirable both from a economic sense (to eliminate hydrocarbons from the reaction media) and a safety and environmental standpoint. In addition, the step of bleaching by hypochlorite and chlorine results in the destruction of the bleach species itself, such that subsequent bleaching requires a fresh supply of the chlorine bleach.

10 Another disadvantage is that certain microorganisms that are intended to be killed by these two commonly-used bleach materials can develop a resistance over time, specifically at lower concentrations of the chlorine or hypochlorite.

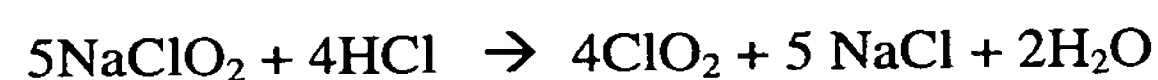
Chloride dioxide is generally used in an aqueous solution at levels up to about 35%. It is a troublesome material to transport and handle at high aqueous concentrations, due to its low

15 stability and high corrosivity. This has required end users to generate chlorine dioxide on demand, usually employing a precursor such as sodium chlorite (NaClO_2) or sodium chlorate (NaClO_3).

A typical process for generating chlorine dioxide from sodium chlorate salt is the acid-catalyzed reaction:



Sodium chlorite is easier to convert to chlorine dioxide. A typical process for generating chlorine dioxide from sodium chlorite salt is the acid-catalyzed reaction:



Further details on the acid-catalyzed reactions of chlorites and chlorates to produce

25 chlorine dioxide can be found in "Chlorine Dioxide Generation Chemistry" (A.R. Pitochelli, Rio Linda Chemical Company), Third International Symposium: Chlorine Dioxide Drinking Water, Process Water and Wastewater Issues, September 14, 15, 1995, La Meridian Hotel, New Orleans, Louisiana, incorporated herein by reference.

A common method of making chlorine dioxide uses a multi-chamber electrolysis cell that

30 converts the chlorite salt into chlorine dioxide. This method uses separately an anode compartment and a cathode compartment that are separated by an ion permeable membrane. The separate compartments operate with significantly different reactants, and contain solutions with different pH values. One example of a multi-compartment electrolysis cell is disclosed in U.S. Patent 4,456,510, issued to Murakami et al. on June 26, 1984, which teaches a process for

forming chlorine dioxide by electrolyzing a solution of sodium chlorite in an electrolysis cell that contains an anode compartment and a cathode compartment separated by a diaphragm, preferably a cation exchange membrane. Another example of a two-chamber electrolysis cell is disclosed in U.S. Patent 5,158,658, issued to Cawlfeld, et al. on Oct. 27, 1992 which describes a continuous electrochemical process and an electrolytic cell having an anode chamber having a porous flow-through anode, a cathode chamber, and a membrane there between.

While separate-compartment, membrane-containing electrolysis cells have been used to make chlorine dioxide on a commercial scale, they have not been completely satisfactory. Even though they may have convenience advantages over the conventional acid catalysis production of chlorine dioxide, the electrochemical approach has proven to be more expensive to produce large volumes of chlorine dioxide. The electrolysis cells in commercial use, and disclosed in the prior art that utilize ion permeable membranes or diaphragms, require that the anolyte solution be substantially free of divalent cations, such as magnesium and calcium, to avoid the formation of precipitated calcium or magnesium salts that would quickly block and cover the membrane, and significantly reduce or stop the electrolysis reaction.

There remains a need for a simple, safe method and apparatus for manufacturing chlorine dioxide to meet a wide variety of commercial and domestic uses, under a wide variety of situations. This need was substantially met via the filing of United States Patent Application Number 09/947,846, filed on 06 September 2001, directed to an Electrolysis Cell for Generating Chlorine Dioxide. Nevertheless, there remains a significant need to identify electrolysis devices and/or cells suitable for interface with common household appliances. Such electrolysis devices and/or cells can be used to disinfect water that is employed and/or dispensed by an appliance, thereby reducing the need for upstream and/or downstream water purification and/or sanitization devices.

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SUMMARY OF THE INVENTION

The present invention relates to apparatuses for making halogen dioxide from an aqueous solution comprising a halogen dioxide salt, using a non-membrane electrolysis cell, in an appliance. A non-membrane electrolysis cell is an electrolysis cell that comprises an anode electrode and a cathode electrode, and having a cell chamber, and which does not have an ion permeable membrane that divides the cell passage into two (or more) distinct anode and cathode chambers. The halogen dioxide salt is converted to the halogen dioxide as electricity passes through the aqueous feed solution in a passage that forms a portion of the cell chamber adjacent to the surface of the anode.

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In present invention further relates to electrolysis apparatuses and/or cells suitable for interface with an appliance. The interface of the electrolytic apparatuses and/or cells disclosed herein with an appliance serves to disinfect and/or sterilize one or more parts of said appliance, the contents of said appliance, and/or water delivered to and/or from said appliance. For purposes
5 of the present disclosure, an appliance is defined as a device designed for home use, comprising a source of electrical or other power necessary for executing the defined functions of the device.

BRIEF DESCRIPTION OF THE DRAWINGS

The various advantages of the present invention will become apparent to skilled artisans
10 after studying the following specification and by reference to the drawings in which:

Fig. 1 shows an electrolysis cell used in the practice of the present invention.

Fig. 2 shows a sectional view of the electrolysis cell of Fig. 1 though line 2-2.

Fig. 3 shows a sectional view of an alternative electrolysis cell used in the practice of the present invention.

15 Fig. 4 is a sectional view of another electrolysis cell having a porous anode.

Fig. 5 is a sectional view of yet another electrolysis cell having a porous anode.

Fig. 6 is a sectional view of another electrolysis cell having a porous anode and a porous flow barrier.

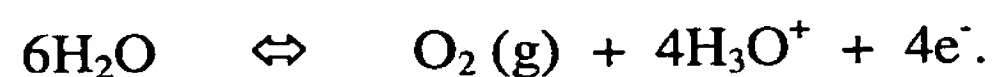
20 Fig. 7 is a sectional view of yet another electrolysis cell having a porous anode and a porous flow barrier.

Fig. 8 is a sectional view of still another electrolysis cell having a porous anode and a porous flow barrier.

DETAILED DESCRIPTION OF THE INVENTION

25 The present invention employs an electrical current passing through an aqueous feed solution between an anode and a cathode to convert the halogen dioxide salt precursor dissolved within the solution into a halogen dioxide. When an aqueous solution flows through the chamber of the electrolysis cell, and electrical current is passed between the anode and the cathode, several chemical reactions occur that involve the water, as well as one or more of the other salts or ions
30 contained in the aqueous solution.

At the anode, within a narrow layer of the aqueous solution in the passage adjacent to the anode surface, the following reaction occurs:



Without being bound by any particular theory, it is believed that the anode electrode withdraws electrons from the water adjacent to the anode, which results in the formation of H_3O^+ species in the narrow surface layer of aqueous feed solution. The H_3O^+ species react with the chlorine dioxide salt, for example, sodium chlorite, to generate chlorine dioxide in the aqueous solution within the passage at the anode surface region. This surface layer is believed to be about 100 nanometers in thickness. Flow dynamics, which include the movement of molecules in a flowing solution by turbulence, predict that the conversion of chlorite salts to chlorine dioxide will increase as the solution flow path nears the anode surface layer. Consequently, electrolysis cells and electrolysis systems of the present invention preferably maximize the flow of the aqueous feed solution through this surface layer adjacent the anode, in order to maximize the conversion of chlorite to chlorine dioxide.

Although the present invention relates to halogen dioxide product and can include iodine dioxide, bromine dioxide and fluorine dioxide, the more common and most preferred product is chlorine dioxide.

The precursor material from which the halogen dioxide is formed is referred to as a halogen dioxide salt. The more common and most preferred halogen dioxide salt is the corresponding halite salt of the general formula MXO_2 , wherein M is selected from alkali and alkali-metal earth metal, and is more commonly selected from sodium, potassium, magnesium and calcium, and is most preferably sodium; and wherein X is halogen and is selected from Cl, Br, I and F, and is preferably Cl. The halogen dioxide salt can comprise two or more salts in various mixtures.

The aqueous feed solution comprises the halogen dioxide salt, which for simplicity will be exemplified herein after by the most preferred halite salt, sodium chlorite. Sodium chlorite is not a salt ordinarily found in tap water, well water, and other water sources. Consequently, an amount of the sodium chlorite salt is added into the aqueous feed solution at a desired concentration generally of at least 0.1 ppm.

The level of chlorite salt comprised in the aqueous feed solution can be selected based on the required bleaching or disinfection required by the chlorine dioxide, in addition to the conversion efficiency of the electrolysis cell to convert the sodium chlorite to the product chloride dioxide. The level of sodium chlorite is generally from about 1 ppm to about 10,000 ppm. For disinfection of a water source, a sodium chlorite level is preferably from about 1 ppm to about 5000 ppm, and more preferably about 10 ppm to about 1000 ppm. The resulting halogen dioxide product level is from about 0.1 ppm to about 10,000 ppm, preferably from about 1 ppm to about

200 ppm. For bleaching purposes, a sodium chlorite level of from about 100 ppm to about 10,000 ppm is preferred.

The range of chlorine dioxide conversion that is achievable in the electrolysis cells of the present invention generally ranges from less than about 1% to about 99%. The level of
5 conversion is dependent most significantly on the design of the electrolysis cell, herein after described, as well as on the electrical current properties used in the electrolysis cell.

The aqueous feed solution can comprise de-ionized water, and substantially no chloride (Cl⁻) or other halide ions, which upon electrolysis can form chlorine or a mixed oxidant, including hypochlorite. Preferably, aqueous effluent comprises less than about 1.0 ppm, and more
10 preferably less than 0.1 ppm, of chlorine.

The aqueous feed solution can optionally comprise one or more other salts in addition to the sodium chlorite. These optional salts can be used to enhance the disinfection and bleaching performance of the effluent that is discharged from the electrolysis cell, or to provide other mixed oxidants in response to the passing of electrical current through the electrolysis cell. A preferred
15 other salt is an alkali halide, that is most preferably a sodium chloride. A preferred apparatus and method for electrolyzing aqueous solutions comprising alkali halides is disclosed in co-pending, commonly-assigned U.S. provisional patent application 60/280,913 (Docket 8492P), filed on April 2, 2001.

The aqueous feed solution comprising the sodium chlorite can be provided in a variety of
20 ways. A solid, preferably powdered, form of the sodium chlorite can be mixed into an aqueous solution to form a dissolved solution, which can be used as-is as the aqueous feed solution or, if in a concentrated solution can be subsequently diluted with water. Preferably, a concentrated solution of about 2% to about 35% sodium chlorite can be used.

The present invention can optionally use a local source of halogen dioxide salt, and a
25 means for delivering the halogen dioxide salt to the aqueous feed solution. This embodiment is advantageously used in those situations when the target water to be treated with the electrolysis cell does not contain a sufficient amount, or any, of the halogen dioxide salt. The local source of halogen dioxide salt can be released into a stream of the aqueous solution, which then passes through the electrolysis cell. The local source of halogen dioxide salt can also be released into a
30 portion of a reservoir of aqueous solution, which portion is then drawn into the electrolysis cell. Preferably, all the local source of halogen dioxide salt passes through the electrolysis cell, to maximize the conversion to halogen dioxide, and to limit the addition of salts to the reservoir generally. The local source of halogen dioxide salt can also supplement any residual levels of halogen dioxide salt already contained in the aqueous solution.

The local source of halogen dioxide salt can be a concentrated brine solution, a salt tablet in fluid contact with the reservoir of electrolytic solution, or both. A preferred local source of halogen dioxide salt is a solid or powdered material. The means for delivering the local source of halogen dioxide salt can comprise a salt chamber comprising the halogen dioxide salt, preferably
5 a pill or tablet, through which a portion of the aqueous solution passes, thereby dissolving a portion of the halogen dioxide salt to form the aqueous feed solution. The salt chamber can comprise a salt void formed in the body of the device that holds the electrolysis cell, which is positioned in fluid communication with the portion of aqueous solution that will pass through the electrolysis cell.

10 In certain circumstances, a preferred halogen dioxide salt has a reduced solubility in water, compared to sodium chlorite, to control the rate of dissolution of the halogen dioxide salt. Examples of preferred halogen dioxide salts are the less soluble calcium chlorite and magnesium chlorite salts. A pill or tablet can also be formulated with other organic and inorganic materials to control the rate of dissolution of the halogen dioxide salt. Preferred is a slow dissolving salt
15 tablet, to release sufficient halogen dioxide salt to form an effective amount of halogen dioxide product. The release amount of the halogen dioxide salt is typically, between 1 milligram to 10 grams halogen dioxide salt, for each liter of solution passed through the electrolysis cell. The halide pill can be a simple admixture of the halogen dioxide salt with the dissolution control materials, which can be selected from various well-known encapsulating materials, including but
20 not limited to fatty alcohol, fatty acids, and waxes..

Any water source can be used to form the aqueous feed solution, including well water, tap water, softened water, and industrial process water, and waste waters. However, for many applications of the invention, distilled or de-ionized water is most preferred to form an effluent solution with essentially only chlorine dioxide active. . Since distilled and de-ionized water do
25 not contain any of a variety of other salts, including sodium chloride, appreciable amounts of other mixed oxidants will not be formed. Even in those situations where one prefers to include other salts, including sodium chloride, in solution with the sodium chlorite, de-ionized water is more preferred, as it allows for better control of the types and amounts of the salts being passed through the electrolysis cell.

30 The addition of other salts or electrolytes into the selected water source will increase the conductivity of the water, which will increase the amount of chlorine dioxide, and any mixed oxidants, produced. However, the increase in conductivity may not result in a higher productivity efficiency, since the increase in conductivity will increase the current draw. Therefore, while

more chlorine dioxide will be produced, more power will be drawn. A suitable chlorine dioxide productivity equation is expressed by equation I,

$$\eta = (\text{CClO}_2 * Q) / (I * V) \quad (I)$$

wherein:

- 5 η units are micrograms of chlorine dioxide per minute, per watt of power used;
 CClO_2 is the concentration of the generated chlorine dioxide in milligrams per liter (mg/l);
 I is the electric current in amps;
 Q is the volumetric flow rate in milliliters per minute (ml/m); and
10 V is electric potential across the cell in volts.

The pH of the aqueous feed solution containing the halogen dioxide salt is preferably above about 3, and more preferably above about 5. If the pH of the aqueous feed solution is too low, the sodium chlorite, for example, can begin to react with the hydronium ions in the feed solution and convert to chlorine dioxide, even before entering the electrolysis cell. The aqueous
15 feed solution is preferably maintained at a pH of less than 10, and more preferably at a pH of less than 8. Most preferably, the pH of the feed solution is between about 6 and 8.

The present invention is particularly well suited for the preparation of aqueous effluents containing chlorine dioxide when the aqueous feed solution is a water source that contains calcium and other divalent salts that can precipitate salts as a by-product of the water electrolysis.
20 Because the present electrolysis cell does not have an ion permeable membrane separating the cell into separate anode and cathode chambers, there is reduced risk that the precipitation of calcium or other divalent salt will inhibit or stop the electrical current flow and the conversion of halite to halogen dioxide.

The aqueous feed solution containing the sodium chlorite can be fed to the electrolysis
25 cell from a batch storage container. Alternatively, the feed solution can be prepared continuously by admixing a concentrated aqueous solution of sodium chlorite with a second water source, and passing continuously the admixture to the electrolysis cell. Optionally, a portion of the aqueous feed solution can comprise a recycled portion of the effluent from the electrolysis cell. And, the aqueous feed solution can comprise a combination of any of the forgoing sources. The aqueous
30 feed solution can flow continuously or periodically through the electrolysis cell.

Electrolysis cell

The electrolysis cell generates chlorine dioxide from the sodium chlorite by flowing electrical current through the aqueous feed solution that passes through the cell chamber. The

electrolysis cell comprises at least a pair of electrodes, an anode and a cathode. The cell also comprises a cell chamber through which the aqueous feed solution passes, and includes a passage that is adjacent to the anode. The passage includes the narrow surface layer adjacent to the anode surface where the conversion reaction occurs. It is preferred to pass as much of the mass of the aqueous effluent solution through the passage and its narrow anode surface region as possible.

In one embodiment of the present invention, the cell comprises an anode and a confronting (and preferably, co-extensive) cathode that are separated by a cell chamber that has a shape defined by the confronting surfaces of the pair of electrodes. The cell chamber has a cell gap, which is the perpendicular distance between the two confronting electrodes. Typically, the cell gap will be substantially constant across the confronting surfaces of the electrodes. The cell gap is preferably 0.5 mm or less, more preferably 0.2 mm or less.

The electrolysis cell can also comprise two or more anodes, or two or more cathodes. The anode and cathode plates are alternated so that an anode is confronted by a cathode on each face, with a cell chamber there between. Examples of electrolysis cells that can comprise a plurality of anodes and cathodes are disclosed in U.S. Patent 5,534,120, issued to Ando et al. on July 9, 1996, and U.S. Patent 4,062,754, issued to Eibl on Dec. 13, 1977, which are incorporated herein by reference.

Generally, the electrolysis cell will have one or more inlet openings in fluid communication with each cell chamber, and one or more outlet openings in fluid communication with the chambers. The inlet opening is also in fluid communication with the source of aqueous feed solution, such that the aqueous feed solution can flow into the inlet, through the chamber, and from the outlet of the electrolysis cell. The effluent solution (the electrolyzed aqueous feed solution that exits from the electrolysis cell) comprises an amount of chlorine dioxide that was converted within the cell passage in response to the flow of electrical current through the solution. The effluent solution can be used as a source of chlorine dioxide, for example, for disinfecting or bleaching articles, or for treating other volumes of water or aqueous solutions. The effluent can itself be a treated solution, where the feed solution contains microorganisms or some other oxidizable source material that can be oxidized *in situ* by the chlorine dioxide that is formed.

The present invention also provides a halogen dioxide generating system, comprising:

- a) a source of an aqueous feed solution comprising a halogen dioxide salt;
- b) a non-membrane electrolysis cell having a cell chamber, and comprising an anode and a cathode, the cell chamber having a passage adjacent to the anode, and an inlet and an outlet in fluid communication with the cell chamber;

c) a means for passing the aqueous feed solution into the cell chamber, along the passage, and out of the outlet; and

d) an electric current supply to flow a current through the aqueous solution in the chamber, to convert a portion of the halogen dioxide salt in the passage to halogen dioxide, and thereby form an aqueous effluent comprising halogen dioxide.

Fig. 1 and Fig. 2 show an embodiment of an electrolysis cell 10 of the present invention. The cell comprises an anode 21 electrode, and a cathode 22 electrode. The electrodes are held a fixed distance away from one another by a pair of opposed non-conductive electrode holders 30 having electrode spacers 31 that space apart the confronting longitudinal edges of the anode and cathode to form a cell chamber 23 having a chamber gap. The chamber 23 has a cell inlet 25 through which the aqueous feed solution can pass into of the cell, and an opposed cell outlet 26 from which the effluent can pass out of the electrolysis cell. The assembly of the anode and cathode, and the opposed plate holders are held tightly together between a non-conductive anode cover 33 (shown partially cut away) and cathode cover 34, by a retaining means (not shown) that can comprise non-conductive, water-proof adhesive, bolts, or other means, thereby restricting exposure of the two electrodes only to the electrolysis solution that flows through the chamber 23. Anode lead 27 and cathode lead 28 extend laterally and sealably through channels made in the electrode holders 30.

Fig. 2 shows cell chamber 23 and the passage 24 along the anode 21 surface. The passage 24 is a portion of the cell chamber 23, though it is shown with a boundary 29 only to illustrate its adjacent to the anode 21, and not to show the relative proportion or scale relative to the cell chamber.

Another embodiment of the electrolysis cell of the present invention is shown in Fig. 3. This electrolysis cell has an anode outlet 35. The anode outlet removes a portion of the electrolyzed feed solution flowing in the passage 24 adjacent the anode 21 as an anode effluent. The remainder of the cell effluent exits from the cell outlet 26, which hereafter will also be referred to as the cathode effluent and the cathode outlet, respectively. Similar electrolysis cells that remove a portion of the electrolyzed solution flowing adjacent the anode through an anode outlet are described in U.S. Patent 5,316,740, issued to Baker et al. on May 31, 1994, U.S. Patent 5,534,120 issued to Ando et al. on July 9, 1996, and U. S. Patent 5,858,201, issued to Otsuka et al. on Jan. 12, 1999. Particularly preferred is an electrolysis cell as shown in Fig. 3 of U.S. Patent 4,761,208 that uses a physical barrier (element 16) positioned between the anode and the cathode adjacent the outlet, whereby mixing of the solution adjacent the anode with the solution adjacent the cathode can be minimized or eliminated prior to removal through the anode outlet. Preferably,

the cathode effluent, which will comprise a low level or no chlorine dioxide product, is passed back to and mixed into the aqueous feed solution.

An electrode can generally have any shape that can effectively conduct electricity through the aqueous feed solution between itself and another electrode, and can include, but is not limited to, a planar electrode, an annular electrode, a spring-type electrode, and a porous electrode. The anode and cathode electrodes can be shaped and positioned to provide a substantially uniform gap between a cathode and an anode electrode pair, as shown in Fig. 2. On the other hand, the anode and the cathode can have different shapes, different dimensions, and can be positioned apart from one another non-uniformly. The important relationship between the anode and the cathode is for a sufficient flow of current through the anode at an appropriate voltage to promote the conversion of the halite salt to halogen dioxide within the cell passage adjacent the anode.

Planar electrodes, such as shown in Fig. 2, have a length along the flow path of the solution, and a width oriented transverse to the flow path. The aspect ratio of planar electrodes, defined by the ratio of the length to the width, is generally between 0.2 and 10, more preferably between 0.1 and 6, and most preferably between 2 and 4.

The electrodes, both the anode and the cathode, are commonly metallic, conductive materials, though non-metallic conducting materials, such as carbon, can also be used. The materials of the anode and the cathode can be the same, but can advantageously be different. To minimize corrosion, chemical resistant metals are preferably used. Examples of suitable electrodes are disclosed in US Patent 3,632,498 and U.S. Patent 3,771,385. Preferred anode metals are stainless steel, platinum, palladium, iridium, ruthenium, as well as iron, nickel and chromium, and alloys and metal oxides thereof. More preferred are electrodes made of a valve metal such as titanium, tantalum, aluminum, zirconium, tungsten or alloys thereof, which are coated or layered with a Group VIII metal that is preferably selected from platinum, iridium, and ruthenium, and oxides and alloys thereof. One preferred anode is made of titanium core and coated with, or layered with, ruthenium, ruthenium oxide, iridium, iridium oxide, and mixtures thereof, having a thickness of at least 0.1 micron, preferably at least 0.3 micron.

For many applications, a metal foil having a thickness of about 0.03 mm to about 0.3 mm can be used. Foil electrodes should be made stable in the cell so that they do not warp or flex in response to the flow of liquids through the passage that can interfere with proper electrolysis operation. The use of foil electrodes is particularly advantageous when the cost of the device must be minimized, or when the lifespan of the electrolysis device is expected or intended to be short, generally about one year or less. Foil electrodes can be made of any of the metals described

above, and are preferably attached as a laminate to a less expensive electrically-conductive base metal, such as tantalum, stainless steel, and others.

A particularly preferred anode electrode of the present inventions is a porous, or flow-through anode. The porous anode has a large surface area and large pore volume sufficient to
5 pass there through a large volume of aqueous feed solution. The plurality of pores and flow channels in the porous anode provide a greatly increased surface area providing a plurality of passages, through which the aqueous feed solution can pass. Porous media useful in the present invention are commercially available from Astro Met Inc. in Cincinnati, Ohio, Porvair Inc. in Henderson, N.C., or Mott Metallurgical in Farmington, CT. Alternately US patents 5,447,774
10 and 5,937,641 give suitable examples of porous media processing. Preferably, the porous anode has a ratio of surface area (in square centimeters) to total volume (in cubic centimeters) of more than about 5 cm^{-1} , more preferably of more than about 10 cm^{-1} , even more preferably more than about 50 cm^{-1} and most preferably of more than about 200 cm^{-1} . Preferably the porous anode has a porosity of at least about 10%, more preferably of about 30% to about 98%, and most preferably
15 of about 40% to about 70%. Preferably, the porous anode has a combination of high surface area and electrical conductivity across the entire volume of the anode, to optimize the solution flow rate through the anode, and the conversion of chlorite salt contained in the solution to the chlorine dioxide product.

The flow path of the aqueous feed solution through the porous anode should be sufficient,
20 in terms of the exposure time of the solution to the surface of the anode, to convert the chlorite salt to the chlorine dioxide. The flow path can be selected to pass the feed solution in parallel with the flow of electricity through the anode (in either the same direction or in the opposite direction to the flow of electricity), or in a cross direction with the flow of electricity. The porous anode permits a larger portion of the aqueous feed solution to pass through the passages adjacent
25 to the anode surface, thereby increasing the proportion of the halogen dioxide salt that can be converted to the halogen dioxide product.

Figure 4 shows an electrolysis cell comprising a porous anode 21. The porous anode has a multiplicity of capillary-like flow passages 24 through which the aqueous feed solution can pass adjacent to the anode surfaces within the porous electrode. In the electrolysis cell of Fig. 4, the
30 aqueous feed solution flows in a parallel direction to the flow of electricity between the anode and the cathode.

Another embodiment of an electrolysis cell having a porous anode is shown in Fig. 5. In this embodiment, the flow of aqueous feed solution is in a cross direction to the flow of electricity between the anode and the cathode. Because the flow passages through the porous anode are

generally small (less than 0.2 mm), the flow of a unit of solution through a porous anode will require substantially more pressure than the same quantity flowing through an open cell chamber. Consequently, if aqueous feed solution is introduced into an electrolysis cell having a porous anode and an open chamber, generally the amount of solution flowing through the porous anode and across its surfaces will be significantly diminished, since the solution will flow preferentially
5 through the open cell chamber.

To address the above problem where the aqueous feed solution can by-pass the porous anode, the cell chamber is preferably provided, as shown in FIG. 6, with a non-conducting, porous flow barrier 40, within the volume of the cell chamber 24 between the cathode 22 and the porous
10 anode 21. The porous barrier 40 is non-conducting, to prevent electricity from short-circuiting between the anode and the cathode via the chamber material. The porous barrier exerts a solution pressure drop as the aqueous feed solution flows through the cell chamber. The porous barrier should not absorb or retain water, and should not react with the aqueous solution and chemical ingredients therein, including the halogen dioxide products. The porous barrier 40 can be made of
15 a non-conducting material selected from, but not limited to, plastics such as polyethylene, polypropylene, and polyolefin, glass or other siliceous material, and silicon. The porous barrier can comprise a plurality of spheres, ovals, and other shaped objects of the same size or of different sizes, that can be packed loosely, or as a unified matrix of articles, into the chamber. FIG. 6 shows the porous barrier 40 as a matrix of spherical objects of varying diameters. The
20 porous barrier 40 can also be a one or more baffles, which substantially restrict the flow of the solution through the cell chamber 24. As shown in FIG. 7, such baffles can comprise a series of vertical barriers having apertures therein for restricting the flow of solution. The restricted flow of aqueous feed solution through the non-conducting, porous barrier significantly reduces the proportion of aqueous feed solution that can pass through cell chamber, thereby increasing the
25 proportion of halogen dioxide salt that is converted in the passages 23 within the porous anode 21.

While the solution flowing through the porous anode and the cell chamber 24 containing the porous barrier 40 can mix and flow back and forth somewhat between each other, the effluents exiting from the different areas of the outlet end 26 of the cell have substantially different solution compositions. The effluent 38 exiting the porous anode will have a significantly lower pH and
30 higher conversion of halogen dioxide product than the effluent 39 exiting the cell chamber adjacent to the cathode. The effluent 38 exiting the porous anode can be separated from the effluent 39 and removed from the cell by placing a barrier 37 as shown in FIG 8.

Another embodiment of the present invention uses an electrolysis cell that has an open chamber. The open-chamber electrolysis cell is particularly useful in the practice of the invention

in reservoirs of aqueous feed solution, including pools, bath tubs, spas, tanks, and other open bodies of water. The aqueous feed solution can flow into the cell and to the anode from various directions. The halogen dioxide salt in the aqueous feed solution can be contained in the reservoir solution, or can be delivered into the reservoir solution locally as a local source of halogen
5 dioxide salt, as herein before described. Examples of open-chamber electrolysis cells include those described in US 4,337,136 (Dahlgren), US 5,013,417 (Judd), US 5,059,296 (Sherman), and US 5,085,753 (Sherman).

An alternative system for generating halogen dioxide comprises a batch container containing the aqueous feed solution. A re-circulating pump circulates the feed solution from the
10 container through an electrolysis cell, and discharges the effluent back to the batch container. In time, the concentration of the un-reacted chlorite salt in the solution will be reduced to essentially zero, whereby the charged amount of sodium chlorite in the aqueous feed solution will have been nearly completely converted to chlorine dioxide product. In a slightly different system, the electrolysis cell can be positioned within the batch container, submerged within the aqueous
15 solution comprising the sodium chlorite. A pump or mixer within the container forces the solution through the electrolysis cell, and re-circulates the solution until the target conversion of sodium chlorite to chlorine dioxide is achieved.

The electrolysis cell can also comprise a batch-type cell that electrolyses a volume of the aqueous feed solution. The batch-type cell comprises a batch chamber having a pair of electrodes.
20 The batch chamber is filled with aqueous feed solution comprising the sodium chlorite salt, which is then electrolyzed to form a batch of effluent solution containing chlorine dioxide. The electrodes preferably comprise an outer annular anode and a concentric inner cathode. An example of a suitable batch cell, for use with a sodium chlorite salt supply in accordance with the present invention, is disclosed in WO 00/71783-A1, published Nov. 30, 2000, incorporated herein
25 by reference.

Electrical Current Supply

An electrical current supply provides a flow of electrical current between the electrodes and across the passage of aqueous feed solution passing across the anode. For many applications,
30 the preferred electrical current supply is a rectifier of household (or industrial) current that converts common 100-230 volt AC current to DC current.

For applications involving portable or small, personal use systems, a preferred electrical current supply is a battery or set of batteries, preferably selected from an alkaline, lithium, silver oxide, manganese oxide, or carbon zinc battery. The batteries can have a nominal voltage

potential of 1.5 volts, 3 volts, 4.5 volts, 6 volts, or any other voltage that meets the power requirements of the electrolysis device. Most preferred are common-type batteries such as “AA” size, “AAA” size, “C” size, and “D” size batteries having a voltage potential of 1.5 V. Two or more batteries can be wired in series (to add their voltage potentials) or in parallel (to add their current capacities), or both (to increase both the potential and the current). Re-chargeable batteries and mechanical wound-spring devices can also be advantageously employed.

Another alternative is a solar cell that can convert (and store) solar power into electrical power. Solar-powered photovoltaic panels can be used advantageously when the power requirements of the electrolysis cell draws currents below 2000 milliamps across voltage potentials between 1.5 and 9 volts.

In one embodiment, the electrolysis cell can comprise a single pair of electrodes having the anode connected to the positive lead and the cathode connected to the negative lead of the battery or batteries. A series of two or more electrodes, or two or more cells (each a pair of electrodes) can be wired to the electrical current source. Arranging the cells in parallel, by connecting each cell anode to the positive terminal(s) and each cell cathode to the negative terminal(s), provides the same electrical potential (voltage) across each cell, and divides (evenly or unevenly) the total current between the two or more electrode pairs. Arranging two cells (for example) in series, by connecting the first cell anode to the positive terminal, the first cell cathode to the second cell anode, and the second cell cathode to the negative terminal, provides the same electrical current across each cell, and divides the total voltage potential (evenly or unevenly) between the two cells.

The electrical current supply can further comprise a circuit for periodically reversing the output polarity of the battery or batteries in order to maintain a high level of electrical efficacy over time. The polarity reversal minimizes or prevents the deposit of scale and the plating of any charged chemical species onto the electrode surfaces. Polarity reversal functions particularly well when using confronting anode and cathode electrodes.

Chlorine Dioxide Effluent

The discharged effluent containing the converted chlorine dioxide is removed from the electrolysis cell and is used, for example, as an aqueous disinfection or an aqueous bleaching solution. The effluent can be used as-made by direct delivery to an oxidizable source that is oxidized by the chlorine dioxide. The oxidizable source can be a second source of water or other aqueous solution comprising microorganisms are destroyed when mixed or contacted with the effluent solution. Microorganisms contained within the aqueous feed solution would also be

destroyed. The oxidizable source can also be an article or object on which oxidizable material is affixed or positioned, such as a kitchen or bathroom surface, including utensils, flatware, plates, sinks, countertops, and the tub and shower areas, appliance surfaces, as well as stains on clothing.

5 The concentrated effluent containing a high concentration of chlorine dioxide can be achieved and maintained by holding the effluent at temperatures below about 5 degrees centigrade, and/or reducing or eliminating sunlight. The effluent can be stored in glass-lined and chemically-resistant plastic surfaced containers.

10 When chlorine dioxide oxidizes an oxidizable material, such as a microorganism or a bleachable stain, the chlorine dioxide releases one of its electron pair and, in the presence of sodium ions, reverts back to sodium chlorite. Because the method and apparatus of the present invention can convert chlorite into chlorine dioxide in simple, non-membrane electrolysis cells, a preferred system for forming chlorine dioxide from an aqueous solution comprises a means for returning the reverted chlorite salts back to the aqueous feed solution, for subsequent re-conversion to chlorine dioxide.

15 The method of making halogen dioxide, according to another preferred embodiment of the present invention, comprises the steps of:

- (1) providing an aqueous supply solution comprising halogen dioxide salt;
- (2) passing a portion of the aqueous supply solution a chamber of an electrolysis cell, preferably a non-membrane electrolysis cell comprising an anode and a cathode, and along a
20 passage adjacent to the anode; and
- (3) flowing an electrical current between the anode and the cathode, thereby electrolyzing the aqueous feed solution in the passage, whereby a portion of the halogen dioxide salt is converted to halogen dioxide, and forming an aqueous effluent comprising halogen dioxide;
- (4) oxidizing an oxidizable material with the converted halogen dioxide in the aqueous
25 effluent, whereby the halogen dioxide reverts back to a halogen dioxide salt; and
- (5) returning the used effluent solution comprising the reverted halogen dioxide salt back to the aqueous supply solution.

30 The oxidizable material can be contacted with the aqueous effluent containing the halogen dioxide in various ways, such as by pouring or spraying the aqueous effluent onto an oxidizable material or an object having an oxidizable material, or by emerging the material or object into the aqueous effluent. The used effluent solution comprising the reverted halogen dioxide salt can be passed through a filter or other type of separator to remove insoluble or particulate matter, before being returned to be used as, or mixed with, the aqueous feed solution.

A preferred embodiment of the present invention comprises halogen dioxide generating and re-cycling system, comprising:

- a) a source of an aqueous feed solution comprising a halogen dioxide salt;
- b) a non-membrane electrolysis cell comprising an anode and a cathode, and having a cell chamber with an inlet and an outlet;
- c) a means for passing the aqueous feed solution into the chamber and along a passage adjacent to the anode, and out of the outlet;
- d) an electric current supply to flow a current through the aqueous solution between the anode and the cathode, to convert a portion of the halogen dioxide salt in the passage to halogen dioxide, and thereby form an aqueous effluent comprising halogen dioxide;
- e) a means for delivering the aqueous effluent into contact with a halogen dioxide depletion target, whereby a portion of the halogen dioxide in the aqueous effluent oxidizes the depletion target and reverts back to a halogen dioxide salt; and
- f) a means for returning the depleted effluent comprising the reverted halogen dioxide salt back to the source.

The means for passing the aqueous feed solution (herein after, "feed means") into the cell can be a pump, or an arrangement where gravity or pressure forces aqueous feed solution from a storage container into the cell. The means for delivering the aqueous effluent into contact with the halogen depletion target can be the feed means, or can be a separate pump or gravity/[pressure arrangement.

The system can also comprise a re-circulation line through which a portion of the effluent solution is returned back to the inlet of the electrolysis cell. As herein before described, re-circulating the effluent back to the cell increases the total conversion of the halogen dioxide salt to the halogen dioxide product.

The means for returning the depleted effluent can be a collection tank with a means, such as any of the feed means, for recycling the depleted effluent back to the source.

Specific Embodiments

In one aspect of the present invention, the electrolytic devices and/or cells disclosed herein are interfaced with an appliance. Suitable appliances for use in conjunction with the present electrolytic devices and/or cells include, but are not limited to: refrigerators, water chillers, water fountains, soda fountains, oral irrigators, water purifiers, water coolers, washing machines, dishwashing machines, coffee makers, faucets and combinations thereof. In one aspect of the present invention, the devices and/or electrolytic cells disclosed herein are incorporated into

and/or interfaced with a refrigerator, in which case the water inlet line connected to said refrigerator is disconnected and instead connected to the inlet an electrolysis device and/or cell described herein. In this aspect of the present invention, the subject electrolytic device may employ an independent source of power (*see* “Electrical Current Supply” section of present disclosure), or alternatively, may be configured to use the electrical current supply of the refrigerator to which it is connected. Those skilled in the art will readily appreciate that there exist several means by which to connect the electrolysis devices disclosed herein to the power supply of a subject appliance, and specifically a refrigerator. Upon connecting the water inlet line to the inlet of the electrolysis device, an outlet line is connected from the outlet of the subject electrolysis device to the vacant inlet of the subject refrigerator. The subject electrolysis device and/or cell may then be operated to electrolyze the water traveling through the water inlet line and into the subject appliance. The above-described configuration will function to eradicate microorganisms present in the water line of the subject refrigerator. The term “water inlet line” is intended to refer to a water line that extends from a main water source in a home or dwelling and is connected to an appliance that uses water.

In one aspect, the concentration of mixed oxidants suitable for use in the context of a refrigerator is from about 0.01 ppm to about 2 ppm, preferably from about 0.1 ppm to about 1.5 ppm, more preferably from about 0.1 ppm to about 1.0 ppm. Without wishing to be bound by theory, it is believed that the aforementioned levels of mixed oxidants are below the taste threshold for human consumers, and thus, undetectable upon consumption of water and/or ice produced from the subject refrigerator.

In yet another aspect of the present invention, the electrolysis devices and/or cells disclosed herein are interfaced with an appliance, and particularly a refrigerator, via placement of the electrolysis device and/or cell at a point along the water line of the subject appliance, and particularly a refrigerator, between the inlet of said appliance and a water dispensing device of said appliance, and particularly a refrigerator. In yet another aspect of the present invention, the electrolysis devices and/or cells described herein are interfaced with a subject appliance, and particularly a refrigerator, via placement of the subject electrolytic device and/or cell at a point along the water line of the subject appliance, and particularly a refrigerator, between the inlet of the subject appliance and an ice-making and/or dispensing device of said appliance.

In one aspect of the present invention, the electrolysis device and/or cell interfaced with an appliance is physically located in the subject appliance. In another aspect of the present invention, the electrolysis device and/or cell interfaced with the subject appliance is physically located outside the body of the subject appliance. In yet another aspect of the present invention,

the electrolytic devices and/or cells disclosed herein are interfaced with a refrigerator, in which case said electrolytic devices and/or cells are refrigerated. In another aspect of the present invention, the electrolytic devices and/or cells described herein are interfaced with a refrigerator via placement of the electrolysis device and/or cell in the refrigerator, yet the subject electrolytic
5 device is not refrigerated.

In yet another aspect of the present invention, the electrolysis devices and/or cells interfaced with an appliance as described herein further comprise a sensor device or similar means for detecting, measuring and/or displaying the level of mixed oxidants generated by the subject electrolysis device and/or cell. In one aspect, a sensor device is placed downstream from the
10 electrolysis device and/or cell. In another aspect of the present invention, the sensor device further comprises a means for controlling the generation of mixed oxidants by the subject electrolysis device and/or cell. In yet another aspect of the present invention, the sensor device comprises a means for increasing and/or decreasing the level of mixed oxidants produced by the interfaced electrolysis device and/or cell. In another aspect of the present invention, the sensor
15 device or similar means comprises a means of controlling the generation of mixed oxidants. Suitable means for controlling the generation of mixed oxidants by the subject electrolysis device and/or cell, include but are not limited to: standard filters, carbon filters and combinations thereof.

It should be noted and underscored that the above recitation of specific embodiments is in
20 no way intended to limit the scope of the present invention. To reiterate, the electrolysis devices and/or cells of the present invention are suitable for incorporation into, and interface with, a variety of appliances. The particular configuration of any such appliance will depend upon several factors, including but not limited to: the nature of the appliance in which incorporation of the present electrolysis devices and/or cells is intended; the specific features and/or power
25 requirements of the subject electrolysis device and/or cell for which incorporation is desired; and the needs and/or abilities of the practitioner. Moreover, although the above disclosure is, in part, directed to the interface of the present electrolytic devices and/or cells with a refrigerator, the devices disclosed herein are suitable for interface with a variety of household appliances. A specific class of household appliances suitable for use in conjunction with the electrolysis devices
30 and/or cells disclosed herein are those appliances associated with a water inlet and/or outlet. Of course, the electrolysis devices and/or cells disclosed herein are particularly effective for placement before and/or after the water inlet of a subject appliance, and are highly effective in eradicating microorganisms from water entering and/or exiting the subject appliance. Other

appliances comprising a water inlet and/or water outlet, though not specifically recited herein, are suitable for use in the context of the present invention.

Examples

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Example 1: *Interface of Electrolytic Device and/or Cell with Household Refrigerator*

The refrigerator includes some form of water inlet whereas the water may be dispensed for drinking via a water dispenser or the water may be frozen for ice making in the freezer compartment. The present electrolysis device and/or cell is placed in line with the inlet water supply either before or after the water line is connected to the refrigerator. The present electrolysis device and/or cell, in or out of the refrigerator, has an inlet port to which the water supply is connected to and an outlet port to which is connected to the refrigerator before the ice maker and water dispenser (see fig 1). The present electrolysis device and/or cell may be placed before the water is chilled, where the water is chilled or after the water is chilled. The present electrolysis device and/or cell may be activated by the icemaker or the water dispenser via an on-off valve. To avoid reducing the volume of useable space for food storage in the refrigerator compartment, the present electrolysis device and/or cell may not be put inside the chilled area of the refrigerator compartment. The present electrolysis device and/or cell may or may not require periodic replacement depending on the making of the device. The present electrolysis device and/or cell may be manually or automatically activated to produce the desired antimicrobial concentration of mixed oxidants. In the case where is in automatically activated, a feedback sensor is placed at or after the outlet port of the present electrolysis device and/or cell and the concentration of the mixed oxidant is adjusted based on the outlet concentration. The adjustment may take place via simple on-off activation, as in a home heating system, or via active sensing and adjustment of the overall power feeding into the present electrolysis device and/or cell. The below diagram illustrates the above-described configuration.

Water inlet line --> EW device --> and/or Ice maker --> ---> Water dispenser-->

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All documents cited are, in relevant part, incorporated herein by reference. The citation of any document herein is not be construed as an admission that the subject reference is prior art with respect to any aspect of the present invention.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to
5 cover in the appended claims all such changes and modifications that are within the scope of this invention.